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ON THE STRUCTURE AND PROPERTIES OF NITROCELLULOSE FROM JUTE FIBRE*

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Plate VII

ABSTRACT. X-ray diffraction patterns of the products obtained by nitrating raw and delignified jute fibres with a mixture of nitric and sulphuric acids have been studied. It has been found that the spacing of the most intense reflection is 7 26 Å. U. in both these cases, but in the latter case the reflection consists of a ring indicating almost random orientation of the micelles in the product. The structure of the products seems to be different from that of nitroramie in both the cases The inflammability and solubility of the products obtained from delignified jute fibre have been found to be different from those of the product obtained from raw jute fibre.

INTRODUCTION

Of all inorganic esters of cellulose, nitrate is the most important, but due to its high inflammability it is gradually being replaced by non-inflammable cellulose acetate. The widespread uses of nitrocellulose covering a wide range of nitrogen are well-known.

The number of hydroxyl groups available for esterification in each C_6 unit is three. When all the hydroxyl groups are reacted upon during nitration a homogeneous product corresponding to cellulose trinitrate is found. Theoretically the completely nitrated cellulose should contain 14.16 per cent of nitrogen but in practice this value has not been obtained. The solubility and other properties which permit its uses in various fields of application depend on the nitrogen content of the nitrated sample.

Cotton, in which cellulose in its purest form is available, is generally used for preparing nitrocelluloses. Miles and Craik (1930), Trogus and Hess (1931), and others have studied thoroughly with the help of X-rays the course of reaction during nitration of cellulose using ramie fibres, the crystallites of which are large and well-oriented, as the source of cellulose. According to Mark (1932 *loc. cit.*) the nitrogroups are distributed statistically along the chains. Trogus and Hess considered the process of nitration as a heterogeneous micellar reaction. Both cotton and ramie fibres contain very high percentages of cellulose but very negligible amount of lignin It is not known, however, whether the product obtained by treating raw jute fibre which contains large percentages of lignin with a mixture of nitric and sulphuric acids is identical

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with that obtained from cotton fibre. Nitration is generally effected by acid mixtures e.g. mixture of nitric and sulphric acids ; and mixture of nitric acid and phosphoric acid, etc. It is quite likely that the lignin is not wholly removed by the action of mixtures of these acids.

The object of the present investigation is to study with the help of X-ray analysis the structure and properties of such a product obtained from jute fibres, and especially to study the influence of lignin present in the fibre on the formation and properties of the end product.

EXPERIMENTAL

Jute fibres cut into small lengths and cleaned by thorough combing were soaked in water for a few minutes. The bundle of fibres was then made free from water by pressing it between filter papers. Concentrated nitric acid about forty times the weight of the fibre was taken in a beaker and then concentrated sulphuric acid of the same volume was added slowly with constant stirring. The bundle of fibres previously soaked in water was then completely immersed in the acid-mixture. After about three minutes the bundle was removed and immersed in a sufficient volume of cold water. Finally the treated sample was washed thoroughly in a stream of running water until it was free from acid. The nitrocellulose thus obtained was pressed between filter papers and allowed to dry. In this method of nitration the fibrous form of raw jute fibre was not destroyed. Cotton and delignified jute fibres were also nitrated by the same method. Delignification of jute fibres was effected by chlorine peroxide. No tension was applied to the fibres during the treatment.

The product obtained from raw jute fibre was light yellow in colour but that from delignified jute fibres was as white as nitrocotton and its fibrous nature was destroyed completely. The sample of nitrojute from raw jute fibre was found to be more inflammable than that obtained from delignified jute fibres, but it was just as inflammable as nitrocotton.

Nitrojute from delignified jute fibre and nitrocotton gave clear solutions in acetone. But when nitrojute from raw jute fibre was dipped in acetone a jelly-like mass was obtained which, when allowed to evaporate on a smooth surface, gave a thin film. The edge of this film was yellowish in colour whereas, the central portion was almost white. It appeared that the latter contained the product from cellulose and the former that from lignin.

Each of these samples was studied with the help of X-rays. Diffraction patterns of nitrated jute and cotton were photographed after making all the strands parallel by pressing them mildly with fingers and holding them taut during the exposure. The X-ray photograph of nitrocellulose from bleached jute fibre was taken using a very thin sheet of the substance, because the product was almost a powder. The photographs were taken in a camera with a very fine slit of 0.5 mm. bore and 5 cm. in length using Cu $K\alpha$ radiation from a Hadding tube and they are reproduced in Plate VI.

The exposure required to obtain the photographs of the diffraction patterns of these nitrated samples was longer than that required for the untreated jute fibre.

RESULTS AND DISCUSSION

In Plate VI, figure 1 represents the diffraction pattern of untreated jute fibre, figure 2 represents that of nitrojute from raw jute fibre, figure 3 corresponds to nitrocotton and figure. 4 is due to nitrojute from delignified jute fibre. For comparison an X-ray photograph of nitroramie obtained by Trogus and Hess (*loc. cit*) is reproduced in figure 5. In Table I are given the spacings of the reflections on the equatorial line of these samples and that of fully nitrated cellulose. These reflections are marked A_1, A_2 and A_3 respectively, starting from the innermost one.

It can be seen from figure 2, that the (101) and ($10\bar{1}$) reflections characteristic of the diffraction pattern due to raw jute fibre (fig. 1) are totally absent in those of nitrated compounds, but a very sharp equatorial reflection of 7·26 Å.U. spacing has appeared. Miles and Craik (*loc. cit.*) have shown that when the nitrogen content of nitroramie is 7·5% or below, the X-ray diagram indicates the presence of hydrated cellulose but with the increase of nitrogen content, the samples give quite different X-ray patterns. The spacing of (002) reflection in raw jute fibre is 3.92 ÅU and that in case of hydrated cellulose from jute fibre as obtained by Sirkar and Saha (1947) is 4.03 ÅU. On careful examination of figures 2, 3, and 4 due to nitrated raw jute, cotton and delignified jute fibres respectively, it is observed that the position of the most intense reflection in all these cases is exactly the same and the spacing of this reflection has been found to be 7.26 ÅU in comparison to 7.41 ÅU in the case of fully nitrated ramie. In the case of hydrated cellulose this ought to have been 7.96 ÅU. Further the sharp reflection from the ($10\bar{1}$) plane of hydrated cellulose was not visible in the patterns obtained with nitrojute.

The X-ray pattern due to nitroramie, (Fig. 5) shows that the most intense equatorial spot is followed by another medium sharp spot and between these two reflections there is a diffuse broad band. According to Miles and Craik (*loc.cit.*), the most intense equatorial spot in the pattern is not constant in position from one sample to other but shows definite shifts corresponding to an increase in spacings as the nitrogen content increases. It appears that the nitrojute obtained in this investigation may be classified into that group containing 10.5% or more of nitrogen and the constant position of the equatorial spot indicates that the degree of nitration in these three cases is same.

It can further be seen from figures 2, 3 and 4, that in the case of nitrocellulose from jute fibre there is no second sharp spot in the equatorial line as in nitroramie (Fig.5) but there are two diffuse bands of spacings 5.05 ÅU and 4.07 ÅU due to amorphous portion in the nitrated samples.

Though the spacing of A_1 reflection in these three cases have been found to be the same there is much difference as to the length and nature of the arc. The length of the arc is greater in case of nitrocotton (Fig.3) than that in the nitrojute (Fig.2), while in the case of nitrojute from delignified jute fibre (Fig. 4), a complete circle is obtained. From this it seems that the orientation of micells in nitrojute (Fig. 2) along the axis of the fibre is of much higher degree than that in nitrocotton. It further appears that the micelles in the product from delignified jute fibre orient themselves almost in a random manner so that the fibrous nature of the product is completely destroyed.

TABLE I

Spacings in Å.U of spots in equatorial line

Sample	A_1	A_2	A_3
Untreated jute fibre	6.05	5.15	3.92
Hydrated (jute)	7.96	1.42	1.03
Nitrojute (Raw)	7.26	5.05 (Band)	1.07 (Band)
Nitrocotton	7.26	5.05 (Band)	1.07 (Band)
Nitrojute (delignified)	7.26	5.05 (Band)	1.07 (Band)
Fully nitrated Ramie	7.41	4.23 (Band)	3.75

The results show that although some properties of nitrojute such as inflammability, solubility and retention of fibrous nature are different from those of nitrocellulose from bleached jute fibre, the X-ray patterns of both the products are identical. Hence lignin does not enter into micells of cellulose-nitrate giving the X-ray patterns. The results are different from those observed in the case of cellulose acetate (Saha, 1947) because the structure of the cellulose acetate obtained from delignified jute fibre was found to be different from that of the same compound obtained from raw jute fibre. It can also be seen from Table I that nitrojute approaches more towards fully nitrated cellulose than hydrated one and the X-ray photographs show no indication of the presence of hydrated cellulose or native cellulose.

So the present investigation leads to conclusion that the nitration is a homogeneous type of reaction though at the beginning the reaction is of micellar surface type as in acetylation of cellulose. The process of nitration as found in this investigation is much quicker than that of acetylation.

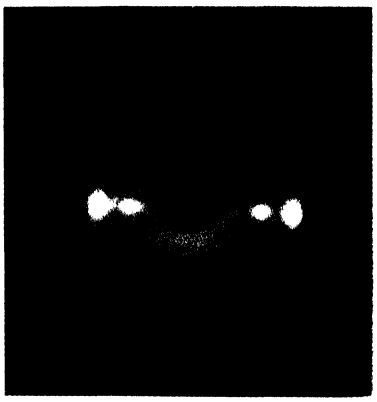

Fig. 1

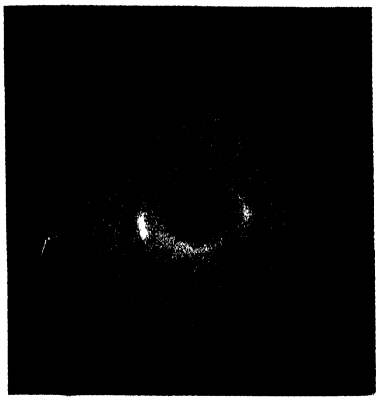

Fig 2

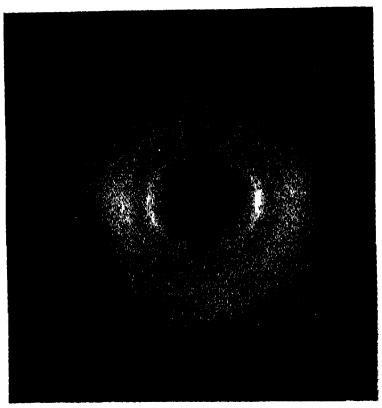

Fig. 3

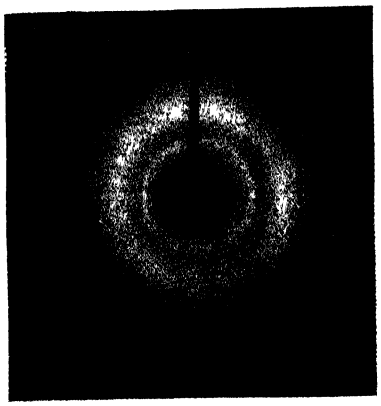

Fig 4

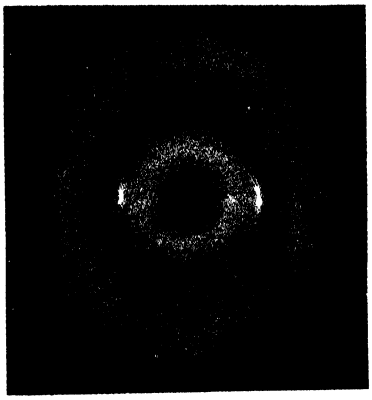

Fig. 5

X-ray diffraction patterns

According to Herzon and Naray Szabo (1927) the diffraction patterns of samples containing 11% to 13% of nitrogen are due to the mixtures of trinitrate and unaltered cellulose. The X-ray diagrams obtained here do not indicate the presence of reflections due to unaltered cellulose. So the results of the present investigation do not support the mixture theory postulated by Herzog, *et al.* It appears that the samples containing about 11-13% of nitrogen are the product of homogeneous nitration.

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